Effects of thermal treatment of activated carbon on the electrochemical behaviour in supercapacitors

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ABSTRACT

This paper studies the electrochemical behaviour of activated carbons with different oxygen content and investigates the contribution of pseudocapacitance to the global behaviour of the samples. A mesophase-derived activated carbon was further heat treated to 600 or 1000°C in nitrogen. The changes in texture and surface chemistry induced by the thermal treatment were deeply studied. The electrochemical behaviour of the samples was studied in two- and three-electrode cells. The contribution of pseudocapacitance was evaluated by cyclic voltammetry and by the differences of specific capacitance obtained from galvanostatic tests performed in acidic (H₂SO₄) and basic (KOH) media. The presence of an extra capacitance due to redox reactions has been proved both in acidic and basic media for the samples with high oxygen content, although its contribution in basic media is significantly lower. The results obtained clearly indicate that the oxygen responsible for CO-evolution participates in redox reactions, whereas the oxygen responsible for the CO₂-evolution is of minor importance.

Keywords: activated carbon, supercapacitors, pseudocapacitance, surface chemistry, surface area.

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INTRODUCTION

Supercapacitors have a significant potential as an alternative or complement to other energy storage or generation devices such as secondary batteries and fuel cells [1]. Carbon materials have been shown as the most attractive electrode materials for these supercapacitors, as a consequence of their relatively low cost, high surface area and availability [2]. In particular, activated carbons obtained by chemical activation of mesophase-derived precursors generally exhibit very good electrochemical performance in this application [3, 4]. In carbon based supercapacitors, energy is stored mainly through the formation of the electrical double layer, although part of the capacitance can be attributed to pseudo-faradaic reactions involving the oxygenated surface groups [5]. However, the surface chemistry of activated carbons is complex and rather different depending on the raw materials and activation conditions and not all the functional groups contribute to pseudocapacitance to the same extent [6-7]. Therefore, it is necessary to investigate the pseudocapacitative phenomena in order to optimise the performance of activated carbons as electrodes in supercapacitors [8-9].

This paper studies the electrochemical behaviour of activated carbons with different oxygen content and investigates the contribution of pseudocapacitance to the global behaviour of the samples. Therefore, a mesophase-derived activated carbon was treated to 600 or 1000°C and the changes in texture and surface chemistry induced by the thermal treatment were deeply studied. The electrochemical behaviour of the samples was studied in two- and three-electrode cells in acidic (H_2SO_4) and basic (KOH) media.

EXPERIMENTAL

Activated Carbons

The naphthalene derived mesophase pitch AR24 was chemically activated using (3:1) KOH to carbon mass ratio, at 700°C for one hour, under a nitrogen flow of 62 mL min⁻¹. The resultant material was neutralized with 1M HCl and then washed with distilled water until pH=7. Finally, the carbon was dried at 110°C in a vacuum oven for 24 h. The resultant activated carbon was labelled AC and was then thermally treated at 600 and 1000°C in a horizontal furnace under a nitrogen flow of 65 mL s⁻¹. The resultant samples were labelled AC-600 and AC-1000, respectively.

Characterisation of Activated Carbons

Physical adsorption of N₂ at 77 K and CO₂ at 273 K was carried out in order to characterise the porous texture of the activated carbons and carbon electrodes. The specific surface area was determined from the N₂ adsorption isotherm using the BET equation. The micropore volume was calculated from the application of the Dubinin-Radushkevich (DR) equation either to the N₂ isotherm (V_{N_2}) or to the CO₂ isotherm (V_{CO_2}). The total pore volume was obtained from the N₂ adsorption at $P/P_0 = 0.99$. The volume of mesopores was calculated by subtracting the total micropore volume (V_{N_2}) from the total pore volume.

The oxygen content of the activated carbons was determined by elemental analysis using a LECO-TF-900 furnace coupled to a LECO-CHNS-932 microanalyser. The surface oxygen functionality was studied by X-ray photoelectron spectroscopy (XPS) using a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyser and a Mg K_α ($h\nu = 1253.6$ eV) X-ray source.

The amount and type of oxygenated surface groups were determined by temperature-programmed decomposition (TPD) under inert atmosphere (He). The sample (150 mg) was

placed in a U-shaped quartz cell and treated at 372 K for 1 h under a He flow of 50 ml/min. Then, the temperature was raised at 10°C/min to 1000°C. On-line mass spectrometry was used to measure the decomposition products (CO and CO₂).

The pH of the activated carbons was determined according to the ASTM D3838-80. The samples were boiled in water using a reflux condenser for 900 s. Then the carbon particles were filtered out and the pH of the filtrate measured after cooling down.

Electrochemical Behaviour

The electrochemical performance of the activated carbons was studied on pellet type electrodes prepared by pressing a mixture of activated carbon (90 wt. %) and PVDF (10 wt. %). The mass of each electrode was about 30 mg. Two-electrode capacitors were built with a glassy fibrous separator and gold current collectors, using a Teflon Swagelok® type system. Tests were performed in 1M H₂SO₄ and 6M KOH. The values of capacitance were estimated from galvanostatic charge/discharge cycling in the voltage range between 0 and 0.8 V at current densities from 0.88 to 88 mA/cm² using a VMP (Biologic, France) multichannel generator. These values were expressed by mass of activated carbon in the smallest electrode. Voltammetry experiments (scan rate of potential from 2 to 10 mV/s) were done in two and three-electrode cells. In the three-electrode configuration, Pt was used as auxiliary electrode and Hg/Hg₂SO₄ or Hg/HgO as reference electrodes and the values of potential are reported versus the normal hydrogen electrode (NHE).

RESULTS AND DISCUSSION

Activated Carbons

The activated carbon AC obtained after chemical activation with KOH is highly microporous, as indicated by the volume of adsorbed nitrogen and the shape of the isotherm (Type I) shown in Figure 1. The textural parameters obtained from the isotherm are summarised in Table 1. The total pore volume of this carbon is 0.85 cm³/g, most of the pores being micropores (88 %), with an average pore diameter of 0.97 nm. The micropore volume estimated from the CO₂ isotherms is significantly lower than that obtained from the N₂ ones, this indicating that the contribution of narrow micropores is negligible. The contribution of mesopores to this sample is rather insignificant (0.10 cm³/g). The microporous surface area and the BET surface area are both very high, as a result of the high volume of micropores present in the sample.

When the activated carbon is treated at 600°C, the total pore volume decreases slightly (Table 1 and Figure 1), the type of porosity remaining essentially the same as for the activated carbon AC. However, when the heat treatment temperature is increased up to 1000°C, the texture of the activated carbon changes more significantly. The decrease of total pore volume and average micropore size is the result of the textural reorganization which occurs during the treatment at higher temperatures.

The data given by elemental analysis, XPS, TPD reveal that the amount of oxygen present in the samples decreases very significantly from AC to AC-600 and AC-1000 (Table 2). The higher values measured by XPS in comparison to elemental analysis indicate that oxygen is mainly located at the surface of carbons. The reduction of the oxygen content caused a significant increase of pH, which varied from 2.8 for AC to 7.3 for AC-1000, suggesting that AC contains carboxylic groups, which are removed after heat treatment up to 1000°C. This is in agreement with the results given by TPD experiments (Table 2). Figure 2 shows the TPD

profiles obtained for the samples, showing the evolution of CO₂ and CO. Upon heating carbon materials, CO₂ evolves at low temperature as a consequence of decomposition of carboxylic groups, lactones or anhydrides [10]. CO evolution occurs at higher temperatures, due to the decomposition of basic or neutral groups such as phenols, ethers and carbonyl groups. For the three activated carbons under study, CO evolved in larger amounts than CO₂. As could be expected when the activated carbon was heat treated at only 600°C, most of the acidic groups were removed, whereas the groups responsible for the CO evolution are still present. After the treatment at 1000°C most of the oxygenated functional groups are removed.

Electrochemical Characteristics

H₂SO₄ as electrolyte

Figure 3 shows an example of the charge-discharge curves obtained for the different samples at 1 mA and that were used to calculate the specific capacitance of the samples. The coulombic efficiency was high for all the samples studied (higher than 99 %). Figure 4 shows the influence of current density on the specific capacitance values determined for the three carbons using a two-electrode cell in H₂SO₄ medium. As could be expected, the sample AC, with the highest pore volume and surface area, demonstrates the highest specific capacitance. Thermal treatment provokes a reduction of capacitance, which is quite important for the sample treated at 1000°C. The decrease of capacitance is significantly larger than it could be expected from the variations of specific surface area/pore volume induced by heat treatment of the samples. Therefore, it is reasonable to assign these changes to the modification of oxygenated surface functionality. It is well known that the presence of oxygenated groups may cause the capacitance to arise from quick Faradaic charge transfer reactions (pseudocapacitance) as well as from electrostatic charging [5]. Hence, some calculations have been made in order to estimate the contribution of pseudocapacitance to the

electrochemical performance of the samples under study. These calculations are just an approximation, as only changes in texture and pseudocapacitance are being considered. Other factors, such as wettability and conductivity, which also influence the total capacitance and are certainly modified by the thermal treatment, were not taken into account.

The decrease of capacitance observed from AC to AC-600 (Figure 4) is proportional to the reduction of microporous surface area (S_{mic}), estimated to 8 %. Then, it can be assessed that the oxygen removed at 600°C, which corresponds to CO₂-evolving groups, does not contribute to capacitance. On the contrary, the specific capacitance of AC-1000 is 36 % lower than for AC, whereas the microporous surface area is only 14 % lower. This mismatch can be related to the removal of CO-desorbing complexes, and consequently to the pseudo-faradaic reactions which are associated to their presence [7]. Hence, pseudocapacitance significantly contributes (~22 %) to the total capacitance of the samples AC in this medium.

The voltammograms obtained in two-electrode cells (Figure 5-a) did not show evidence of pseudocapacitance. On the contrary, pseudocapacitance was clearly observed when cyclic voltammetry was performed in the three-electrode configuration (Figure 5-b). Well-defined redox humps are shown by the AC-electrode. These peaks are significantly smaller for AC-600 and almost negligible for AC-1000. These results are in agreement with the results discussed above in relation to the role of the CO evolving groups (carbonyl or quinone- type groups) in the enhancement of capacitance. Moreover, the voltammograms show that the redox reactions occur both in the anodic and cathodic regions which means that this pseudocapacitance is readily used in a symmetric supercapacitor.

KOH as electrolyte

The electrochemical characteristics of the samples were also studied in basic medium (KOH 6M) (Figure 6 and 7). The specific capacitance of sample AC was slightly higher than that of AC-600, and significantly higher than that of AC-1000 (Figure 6), a similar trend to that observed in sulphuric medium, although, the values of the first two samples are lower in KOH (about 16-18 % lower). According to the voltammograms obtained in the three-electrode configuration (Figure 7-b), the specific capacitance is comparable to the values obtained in sulfuric acid. However, in the alkaline medium the redox reaction of surface groups shifts to negative potentials. In the two-electrode configuration, the capacitance of the whole device is limited by the electrode with the lowest performance, which is the positive one, as can be seen in Figure 7-b. This explains the lower capacitance values obtained in KOH than in H₂SO₄.

Similar calculations to those discussed before for sulfuric medium were done for results obtained in KOH (Figure 6) in order to evaluate the contribution of pseudocapacitance. The decrease in capacitance from AC to AC-600 is around 8 % and, therefore, proportional to the reduction of microporous surface area (similar to that observed in sulphuric medium). Meanwhile, the decrease in capacitance observed for AC-1000 is larger than the reduction in microporous surface area (25 % vs. 14 %). Therefore, it can be estimated that in KOH media about 11 % of the total capacitance of sample AC is due to pseudocapacitance, giving a clear evidence of the presence of pseudocapacitance also in KOH medium for samples AC and AC-600. However, its contribution to the total capacitance is less than in sulphuric medium. The presence of pseudocapacitive phenomena in basic media is not so frequently described in the literature as in acidic media. Zuleta *et al.* [9] have suggested a reversible redox system involving phenol or quinone groups as responsible for the enhancement of the total capacitance.

CONCLUSIONS

The thermal treatment of the mesophase-derived activated carbon at 600°C caused slight changes in texture accompanied by a significant reduction of oxygen content, mainly corresponding to CO₂-evolving groups. The capacitance values of AC and AC-600 are in accordance to the textural differences but are not affected by the modifications of the surface functionality. When the sample is further heat treated to 1000°C, the capacitance values are significantly lower, not only due to the decrease of specific surface area but also to the removal of CO-evolving groups, responsible for pseudo-faradaic charge transfer reactions. The existence of an extra capacitance due to redox reactions has been proved both in acidic and in basic media for samples with high oxygen content. However, in basic media, part of the possible capacitance of the material is misused in a symmetric configuration. The contribution of pseudocapacitance in the two-electrode system has been estimated in about 22 % in acidic media and 11 % in basic media.

Acknowledgements

This work has been performed with financial support from MEC (project MAT2004-03480-C02) and FICYT (project IB05-086-C1). V. Ruiz acknowledges a predoctoral research grant from FICYT. The authors would like to thank University of Alicante for the XPS analyses.

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TABLE CAPTIONS

Table 1.- Textural characterisation of activated carbons

Table 2.- Physicochemical characterisation of the activated carbons.

TABLE 1: Textural characterisation of activated carbons.

Sample	V_T	V_{N_2}	V_{CO_2}	V_{meso}	L_0	S_{mic}	S_{BET}	% micro
AC	0.85	0.75	0.58	0.10	0.97	1531	2008	88
AC-600	0.80	0.70	0.52	0.10	1.00	1407	1884	87
AC-1000	0.66	0.60	0.51	0.06	0.91	1318	1605	91
V_T , total pore volume (cm^3/g) V_{N_2} , total micropore volume (cm^3/g) V_{CO_2} , micropore volume (cm^3/g) V_{meso} , mesopore volume (cm^3/g)				L_0 , average pore diameter (nm) S_{mic} , microporous surface (m^2/g) S_{BET} , BET surface area (m^2/g) % micro, microporosity percentage				

TABLE 2: Physicochemical characterisation of the activated carbons.

Sample	O (wt %)	O (%) XPS	pH	TPD	
				CO (mmol/g)	CO ₂ (mmol/g)
AC	3.54	8.12	2.8	1.223	0.225
AC-600	1.51	5.50	5.5	1.124	0.096
AC-1000	0.33	2.48	7.3	0.134	0.080

FIGURE CAPTIONS

Figure 1.- N₂ adsorption/desorption isotherms of activated carbons.

Figure 2.- TPD profiles of activated carbons: a) CO₂ evolution and b) CO evolution.

Figure 3.- Charge and discharge profiles of samples at 1 mA.

Figure 4.- Variation of specific discharge capacitance with current density in 1M H₂SO₄.

Voltage window = 0.8 V.

Figure 5.- Cyclic voltammetry performed at 2mV/s in a) two-electrode and b) three-electrode cell using H₂SO₄ 1M as electrolyte.

Figure 6.- Variation of specific discharge capacitance with current density in 6M KOH.

Voltage window = 0.8 V.

Figure 7.- Cyclic voltammetry performed at 2mV/s in a) two-electrode and b) three-electrode cell using 6M KOH as electrolyte.

Figure 1

a)

b)

Figure 2

Figure 3

Figure 4

a)

b)

Figure 5

Figure 6.-

a)

b)

Figure 7.-